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Surface stress calculation for one-monolayer adsorption of As on the Si(001) and the Ge(001) surfaces

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Abstract : We report a surface stress calculation for one-monolayer adsorption of As on the Si(001) and the Ge(001) surfaces. The density functional theory within local density approximation has been used. A comparison of our two results show that the As-adsorbed-Ge surface is more isotropic than the As-adsorbed-Si surface. The adsorption of As removes the original Si (Ge) asymmetric dimers and forms symmetric dimers. This is attributed to the decrease in stress anisotropy due to the introduction of defects on the surface. This inference is in agreement with that of He and Zhang who studied a Sb-adsorbed-Si(001) surface.

Keywords : Surface stress, adsorption, arsenic, germanium, silicon, density functional theory, stress anisotropy.

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The adsorption of group-V elements on the surfaces of group-IV elements has been the subject of great interest both theoretically and experimentally in the last few years. The interest has grown because of the influence of group-V elements in enhancing the abruptness of the interface in crystal growth of heterostructures by acting as surfactants, and in modifying the electronic properties by acting as dopants [1]. The adsorption of As, under good experimental conditions leads to a well ordered symmetric dimer structure on both Si(001) and Ge(001) structure [2,3]. Arsenic lowers the surface free energy of both Ge and Si, and it can be used as surfactant in the growth of Si on Ge(001) [4]. The surface stress has been recognized to play important role in the adsorption process of As on Si(001) and Ge(001) surfaces [5,6]. In this paper we report our study of the surface stress calculation of 1-mono-layer adsorption of As on the

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Si(001) and Ge(001) surfaces employing an *ab initio* pseudopotential method.

In this study we have used the density functional theory of Hohenberg, Kohn and Sham (HKS) [7–9] with the utility of the ABINIT code which in based on pseudopotential and plane waves [10]. The electron-ion interaction was included in the form of norm-conserving pseudopotential [11] that are fully separable in the Kleinman-Bylander form [12]. The pseudopotentials were generated using the FHI98pp code [13]. The electron-electron interaction was considered within the local density approximation using the correlation scheme of Perdew and Wang [14].

A brief outline of the density functional theory is given below.

This theory puts charge density at the centre stage. The solution of Schrödinger equation in an external potential would result in a certain ground state wave function Ψ to which is associated a certain charge density

$$\rho(r_1) = \sum M \int |\Psi(x_1, x_2 \ldots\ldots\ldots x_m| \, dx_1, dx_2 \ldots\ldots\ldots dx_m) . \tag{1}$$

Further, there is a certain energy functional which is minimized by the unknown ground charge density, ρ. The Kohn-Sham energy functional is formally written in the form

$$H_{ks} = \hbar^2/2m \cdot \nabla^2 + V_{eff} \tag{2}$$

where the effective potential is defined as for a one-electron potential

$$V_{eff} = V_N(\rho) + V_H(\rho) + V_{XC}(\rho) \tag{3}$$

The energy term associated with the nuclei-electron interaction is $\langle V_N \mid \rho \rangle$ while that associated with the electron-electron interaction is $\langle V_H \mid \rho \rangle$ where V_H is Hartree potential.

$$V_H = \int \rho(r')/|r - r'| \cdot dr' . \tag{4}$$

The Kohn-Sham energy functional is written as

$$E(\rho) = (-\hbar^2/2m) \sum_{i=1}^{N} \int \Phi_i^*(r) \nabla^2 \Phi_i(r) dr + \int \rho(r) V_{ion}(r) dr$$

$$+ 1/2 \iint \rho(r)\rho(r')/|r - r'| \cdot dr dr' + E_x \{\rho(r)\} . \tag{5}$$

Within local density approximation the exchange energy is expressed as

$$E_x \{\rho(r)\} = \int \rho(r) \sum\nolimits_x [\rho(r)] \, d^3r \tag{6}$$

where E_x $[\rho(r)]$ is the exchange energy per particle of a uniform gas at a density of ρ. The exchange potential can be determined from the functional derivative of $E_x[\rho(r)]$

$$i.e.\ V_x(\rho) = \delta E_x(\rho)/\delta\rho . \tag{7}$$

Using Hartree-Fock theory it has been shown that the exchange energy of a free

electron gas is given by

$$E_{HF}^{FEG} = 2\sum_{K<Kf} \hbar^2 k^2/2m$$

$$-(e^2 k_f/\pi)\sum_{K<Kf}\left[1+\left\{\left\{1-(k/k_f)^2\right\}/2(k/k_f)\right\}\ln\left|(k+k_f)/(k-k_f)\right|\right. . \tag{8}$$

Comparing with HF expression for the exchange energy of a 'free electron gas' one obtains for the potential

$$V_x(\rho) = -(e^2/\pi)\cdot\left\{3\pi^2\rho(r)\right\}^{1/3} . \tag{9}$$

Correlation energies can be included in the energy functional, having the form in LDA

$$V_{xc}\left\{\rho(r)\right\} = V_x\left\{\rho(r)\right\} + V_c\left\{\rho(r)\right\} \tag{10}$$

where V_c represents the contribution to the total energy beyond HF limit. Spin is included as

$$\rho = \rho\uparrow + \rho\downarrow$$

where $\uparrow$ and $\downarrow$ represents 'up' and 'down' spins.

The Kohn-Sham equation for the electronic structure of matter is given by

$$\left(-h^2\nabla^2/2m + V_N(r) + V_H(r) + V_{XC}\left[\rho(r)\right]\right)\Phi_i(r) = E_i\Phi_i(r) . \tag{11}$$

The KS equation is solved in LDA by using pseudopotential. The pseudopotential model treats matter as a sea of valence electrons moving in a background of ion cores composed of nuclei and inert inner electrons.

The KS equation must be 'discretized' *i.e.* be reduced from a virtually infinite-unknown problem to a finite-unknown problem. For crystals, plane wave basis has been quite effective.

The plane wave used is of the following form.

$$\Psi_k(r) = \sum_G \alpha(\boldsymbol{k}.\boldsymbol{G})\exp(i/\left|\boldsymbol{k}+\boldsymbol{G}\right|\cdot\boldsymbol{r}) \tag{12}$$

where $\boldsymbol{k}$ = wave vector and it is a quantum number represented as $k = k_1, k_2, k_3$,

$\boldsymbol{G}$ = reciprocal lattice vector and

α $(\boldsymbol{k}.\boldsymbol{G})$ = co-efficient of basis.

When expressed in a plane wave basis, the Hamiltonian is actually dense matrix. Specifically, the Laplacian term of the Hamiltonian is represented by diagonal matrix and the potential term gives rise to a dense matrix.

For non-periodic systems the plane wave basis is combined with a 'super cell' method. The super cell repeats the localized configuration to impose periodicity to the systems. This preserves the "artificial" validity of $\boldsymbol{k}$ and Bloch's theorem which eq. (12) obeys.

For the surface stress calculations we considered a symmetrical unit cell which included an atomic slab with five layers of Ge(Si) and mono-layer of As on each surface. The vacuum region between slabs was taken to be about five mono-layers in thickness. All of the atoms were allowed to relax except the two Ge(Si) layers in the middle of the slab. This choice of slab thickness was found to be adequate as the main contribution to the surface stress come from the first three atomic layers. Single particle wave functions were expanded with a plane wave basis upto a kinetic energy cut off of 12 Ry. The integration in the Brillouin Zone was performed using 8 special k points sampled within the Monkhorst pack scheme [15].

We considered three adsorption sites for the adsorbate As atom : (a) the non-diffused configuration, (b) 50% inter diffusion of As into the 2nd substrate layer and (c) 100% interdiffusion of As into the 2nd substrate layer *i.e.* As-atomic-layer replacing the top Ge(Si) atomic layer. The calculated bond lengths are : As-As $\approx$ 0.252 nm, As-Ge $\approx$ 0.250 nm, Ge-Ge $\approx$ 0.244 nm, As-Si $\approx$ 0.247 nm, Si-Si $\approx$ 0.250 nm.

For computing the surface stress for each of the three As adsorbed surface geometries the following three dimensional stress tensor expression was employed.

$$g_{\alpha\beta} - (C/2)\cdot\sigma_{\alpha\beta}^{\text{corr}} = (C/2)(\sigma_{\alpha\beta} + \chi\delta_{\alpha\beta}) \tag{13}$$

where C is the height of the supercell, χ is the finite basis correction, and $\sigma_{\alpha\beta}$ the three dimensional supercell stress tensor. The results of the present calculation are given in the Table 1. These result show that the lowest energy configuration of (a) is characterized by stress which is compressive along the surface dimer row direction and tensile in the orthogonal direction. A comparison of our two results show that the As-adsorbed-Ge surface is more isotropic than the Si-adsorbed-Ge surface. The total-energy minimization calculations show asymmetric dimers for Si(001) and Ge(001). The adsorption of As removes the original Si(Ge)-dimer reconstruction and forms symmetric dimers [16,17]. This is attributed to the decrease in stress anisotropy due to the introduction of defects on the surface. This inference is in agreement with that of He *et al* [18] who studied a Sb-adsorbed-Si(001) surface.

Table 1. Calculated surface stress in (eV/(1 x 1) unitcell), for direction both perpendicular ($g\perp$) and parallel ($g_{\|}$) to dimer. The differences ($g_{\|} - g\perp$) represent the stress anisotropy.

	As/Si				As/Ge		
	($g\perp$)	($g_{\|}$)	($g_{\|} - g\perp$)		($g\perp$)	($g_{\|}$)	($g_{\|} - g\perp$)
As-capped (a)	–0.59	0.67	1.26	As-capped (a)	–0.38	0.75	1.13
2nd layer (b)	–0.85	0.34	1.19	2nd layer (b)	–0.47	0.32	0.79
Si-capped (c)	–0.92	–0.15	0.77	Ge-capped (c)	–0.61	–0.09	0.52

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References

[1] L H Chan and E I Altman *Phys. Rev.* **B63** 195309 (2001)

[2] P Krüger and L Pollman *Appl. Phys.* **A59** 487 (1994)

[3] J F Morar, U O Karlsson, R I G Uhrberg, J Kanski, P O Nilsson and H Qu *App. Surf Sc.* **41/42** 312 (1980)

[4] M Copel, M C Reuter, M V Hoegen and R M Tromp *Phys. Rev.* **B42** 11682 (1990)

[5] R M Tromp, A W Denier van der Gon and M C Reuter *Phys. Rev. Lett.* **68** 2313 (1992)

[6] R M Tromp *Phys. Rev.* **B47** 7125 (1993)

[7] P Hohenberg and W *Kohn Phys. Rev.* **B136** 864 (1964)

[8] W Kohn and L J Sham *Phys. Rev.* **A140** 1133 (1965)

[9] R M Dreizler and E K U Gross *Density Functional Theory* (Berlin Springer-Verlag : Heidelberg) (1990)

[10] J Nogami, A A Baski and C F Quale *Appl. Phys. Lett.* **58** 475 (1991)

[11] D R Hamann *Phys. Rev.* **B40** 2980 (1989)

[12] L Kleinman and D M Bylander *Phys. Rev. Lett.* **48** 1425 (1982)

[13] M Fuchs and M Scheffler *Comp. Phys. Commun.* **119** 67(1999)

[14] J P Perdew and Y Wang *Phys. Rev.* **B45** 13244 (1992)

[15] H J Monkhorst and J D Pack *Phys. Rev.* **B13** 5188 (1976)

[16] John P LaFemina *Surface Science Reports* **16** 133 (1992)

[17] M E Gonzalez-Mendezand Takeuchi *Bhys. Sat. Sol.* **B220** 79 (2000)

[18] Yao He, X H Zhang and J G Che *Phys. Rev.* **B66** (2002)